I. 20.

DALTON ON SULPHURIC ETHER *Manchester*, 16 April 1819.

Title: Memoir on sulphuric ether. By John Dalton. *Annals of Philosophy*, Feb. 1820, *15*, 117-133. (Issued also in *Memoirs and Proceedings, Manchester Literary and Philosophical Society*, 1820, *n.s.3*, 446-482.

Note: Although Dalton had studied ether in 1805, this is the classic paper on the chemistry and physical properties of sulphuric ether. Henry in his Dalton *Memoirs* (London, 1854) says of it: "He describes the modes he employed to separate ether from the alcohol, which passes over with it in distillation, and which seems to have been sufficiently careful. For he obtained an Ether of the same specific gravity .720, and the same boiling point 95° or 96°, as are now assigned to that fluid. By an earlier experiment in 1805, he had deduced for the specific gravity of its vapour the number 2.65, a fair approximation to 2.586, the number now received. But in this memoir he 'thinks 3.1 is probably the nearest expression in two places of figures that can be obtained.' . . . He performed the analysis of ether by firing its vapour mixed with oxygen, in the proportion of not more than 3 to 10 per cent. of the volume of oxygen, in a Volta's eudiometer. 'This method,' he observes, 'I discovered in September 1803, and have used it occasionally ever since.' "

ful examination of the concretions in the substance of the lungs, Mr. Burns ascertained that each was lodged in a bronchial cell, and was enveloped in a distinct capsule, which admitted of being readily separated from the membrane of the air cell. Indeed in all concretions discovered in the soft parts of the body, Mr. Burns informed me that he has uniformly found a peculiar substance containing the solid substance, and over this another sheath of dense membrane. The inner covering he supposed to belong essentially to the concretion, and the outer one to be formed in consequence of the irritation caused by the presence of an extraneous body.

Calculi from the Spleen.—For the opportunity of examining these, I was indebted to the same zealous and able anatomist. They were of small size, shaped like a pear, of a yellowish-white colour, and were composed of bone earth, without any portion of the triple phosphate.

Small Crystals formed on the Surface of a cancerous Preparation, kept in Spirit of Turpentine.—These also I received from Mr. Burns; and though not strictly belonging to the class of morbid concretions, I mention them here on account of their singular composition. They are in very minute parallelopipedons, are fusible when placed on a piece of iron heated below redness, and evaporate in an aromatic smoke. They are very sparingly soluble in water, but more so in alcohol; and the latter solution, when concentrated, reddens litmus paper. They agree, therefore, in their properties with the camphoric acid, and furnish an instance of the production of that acid under circumstances not before observed. Whether they had passed through the intermediate state of camphor, which, by well known treatment, may be obtained from spirit of turpentine, it is now impossible to ascertain. Mr. Burns, however, assured me that they may not unfrequently be seen on preparations kept in that fluid; but never, except when the parts have been imperfectly dried before being immersed in it. It is probable, therefore, that they may be found under similar circumstances in other anatomical collections.

Manchester, Dec. 16, 1818.

Article V.

*Memoir on Sulphuric Ether.** By John Dalton.

In my essay on the force of steam, read before the Society in 1801, and published in the fifth volume of the Memoirs, I stated some experiments on the force of vapour from sulphuric ether,

* Read before the Literary Society at Manchester, April 16, 1819.

at different temperatures, as exhibited in a Torricellian vacuum, also the force of the same when admitted into a limited portion of air. From these experiments, as well as from corresponding ones made with water, alcohol, and other fluids, I was led to adopt the important conclusion, that steam acquires the same force in air as in a vacuum, and that it ought to be considered the same independent fluid in both cases. Consequently if p denote the pressure of any given volume of air (1), and f denote the pressure of steam of a given temperature, such steam being admitted to the air, the volume of both in due time becomes $\frac{p}{p-f}$.

This theorem is most beautifully illustrated by sulphuric ether. Let a common barometer have a drop of ether let up into the vacuum; it will instantly depress the mercury several inches, more or less according to the temperature. Suppose it were 10 inches, the barometer being 30; then $\frac{p}{p-f} = 1{\cdot}5$; that is, if ether be passed up into air under those circumstances, it will in due time increase the volume of air 50 per cent.

For six years after this I was occasionally engaged in the further investigation of the nature and properties of ether, in which several additional facts, and some corrections of those antecedently announced, occurred. The combustion of ether was effected in various ways, as well as its analysis, by heat and by electricity.

During all this time I procured my ether in small quantities at a time, and of various druggists, as suited my convenience. Once or twice I ascertained the specific gravity of the article to be at or near 0·75; and I never found reason to suspect there was much difference in the specimens. Occasionally when great part of the ether was evaporated by time and neglect, I found a few drops at the bottom of the phial, which did not possess the properties of ether, but this was too small to be much regarded. In an excursion to Edinburgh and Glasgow in 1807, I exhibited the steam of ether, as above described, to a few persons in those two places; when at the latter place, Dr. Ure was so good as to supply me with ether, but upon trial it did not present the properties I had usually recognized, which at the time I attributed to accidental impurities, acquired in the laboratory; upon this he accompanied me to a druggist, where I was immediately supplied with ether of the requisite purity. I apprehend Dr. Ure's ether must have been the *spiritus ætheris sulphurici* of the Edinburgh college, made by adding two parts alcohol to one of ether; or perhaps ether not rectified.

In 1808 I published the first part of my New System of Chemical Philosophy, in which I digested all the knowledge I then had on the force of steam from ether in a tabular form. I had acquired from actual observation the forces in a range of tem-

perature from 0° to 212°. In my former publication I had concluded that the variations in the force of steam from water and ether were the same for the same intervals of temperature; that is, if the force of steam from water was diminished from 30 to 15 inches of mercury, by a diminution of temperature of 30°; then that of ether would be diminished from 30 to 15 inches by the same number of degrees, though in a much lower part of the scale; the former being from 212° to 182°, and the latter from 98° to 68°. Subsequent experience, however, led me to apprehend that the above intervals of temperature, though expressed by equal expansions of mercury, are not in reality equal intervals; but that equal intervals are rather denoted by the forces of steam being in geometrical progression. Consistent with this view I found that steam from water and ether would concur, for a long range of temperature, with the difference of ratios only; that of water being 1·321 for 10° of temperature, whilst that of ether was 1·2278.

In the above work occurs the following observation: "Ether, as manufactured in the large way, appears to be a very homogeneous liquid. I have purchased it in London, Edinburgh, Glasgow, and Manchester, at very different times, of precisely the same quality in respect to its vapour." This observation, though warranted from my limited experience at the time, I now find not altogether correct; I am sorry that it has occasioned an ingenious experimentalist to be led into a labyrinth of error.

The bulk of the ether used in this country has I find of late years been prepared by one manufacturing house in the neighbourhood of London. Three qualities of the article are made according to the different uses intended. The highest quality is only made for particular purposes, and is, therefore, not very commonly met with; it is about 0·73 specific gravity; the second quality is that intended for medicine; it is of 0·75 specific gravity, and is that with which all the country druggists and apothecaries are or ought to be supplied as a standard uniform article; it is that which I have always met with in the shops, and which I have taken for genuine ether in my former experiments. The third quality is of the specific gravity 0·78 or 0·79 usually; of course it is much inferior to the last in purity. But it may be proper to observe, that this is the first state of the other two qualities; they being produced from this by ulterior processes called *rectification*.

It is well known that sulphuric ether is procured by distilling a mixture of sulphuric acid and alcohol. The proportions usually prescribed are equal weights of concentrated acid and alcohol. By due management, a liquid of the specific gravity 0·785 or 0·79 is obtained, called ether. It is the ether of the third quality, just mentioned, and is in fact a compound of

alcohol and ether chiefly, in proportions to be investigated hereafter. In this state it is usually called *unrectified* ether.

When this last liquid is redistilled by a moderate heat till one half has passed over, the liquid in the receiver is denominated *rectified* ether. It is usually about 0·75 specific gravity, corresponding to the *second* quality. It still consists of ether and alcohol, but with much less alcohol than before. There is great reason to believe that both the *unrectified* and *rectified* ether, as thus prepared, are destitute of water, except so far as it is an essential element of the two liquids, ether and alcohol in their purest states; the sulphuric acid being well able to retain all the excess of water of common alcohol in the temperatures employed in the two distillations.

Ether of the first quality, or that in its purest state is to be obtained from the rectified ether just mentioned. The object is to abstract the alcohol still remaining in the rectified ether. This may be done in great part by repeated distillations; always taking the first produce and setting aside the remainder for other use; but this method is tedious and expensive. A more ready method is to agitate the rectified ether with about its own bulk of pure water; after agitation the mixture resolves into two fluids, a heavier and a lighter; the lighter may be decanted, and will be found about two-thirds of the volume of ether used; it will have the specific gravity 0·73 nearly, and may be considered as ether of the first quality. But it is demonstrable that it still contains *some* alcohol, and has besides acquired a portion of water from this process. The watery stratum below contains the greatest part of the alcohol, and has also taken along with it a portion of ether, as is evident from the smell, which is much the same as that of ether itself. This heavy liquid has the specific gravity of 0·96 or 0·97 usually. If this ether of 0·73 specific gravity be again treated with water, it will be reduced nearly to 0·72 specific gravity; but it still contains minute portions of both alcohol and water, the quantities of which are not easily appreciated. Subsequent distillation would doubtless improve the quality a little; but for most practical purposes there is reason to believe that no material difference would be found between the above and ether of absolute purity.

Having obtained ether of the specific gravity 0·72, and alcohol of 0·83 specific gravity, both of which may be considered as very nearly pure or free from water; mixtures of these two liquids may be made in any proportions, and the resulting specific gravities ascertained; from which we may be enabled to estimate the proportions of the two fluids in any specimen where no water is present.

This operation, however, is more difficult than may be imagined. By taking ether and diluting it successively with equal portions of alcohol, the resulting specific gravities may be

found in the usual way, provided we could guard against any loss of the mixture. But such is the evaporating power of ether, especially when pure, that it is impossible to pour it from one vessel into another in the open air without much loss. In one instance I found that after six successive dilutions and 12 transfers, made with great care, I had lost one-fifth of the whole weight used. In such case, if the diluting portions are not diminished duly, the results must be erroneous. One circumstance is favourable, the increase of density by chemical action appears to be very small; so that the densities may be *calculated* without very material error. The following table will afford a moderately good approximation, which may have its use till a better is made.

Table of the Specific Gravities of Mixtures of Ether and Alcohol.

Ether.		Alcohol.	Sp. Gr.
100	+	0	0·720
90	+	10	0·732
80	+	20	0·744
70	+	30	0·756
60	+	40	0·768
50	+	50	0·780
40	+	60	0·792
30	+	70	0·804
20	+	80	0·816
10	+	90	0·828
0	+	100	0·830

From this table it would seem that ether of the second quality, or that of the shops in general, contains about 25 per cent. of alcohol; and that of the third quality from 55 to 60 of alcohol; and the proportion of this article will be still greater on the probable supposition that pure alcohol is as low as 0·82 in specific gravity.

So far we have considered the mixtures of ether and alcohol in their purest states, or nearly such; and it has been observed that in the ordinary course of manufacture, it is these mixtures, only varied in proportion, that occur. But if we introduce water so as to vary the proportions of ether, alcohol, and water, indefinitely, then some new phenomena occur, and the quantity of ether in such mixtures is no longer to be determined by the specific gravities. These mixtures are in some proportions uniform throughout; in others, they resolve into two fluids of different specific gravities, alike transparent and colourless, but easily distinguishable from a filmy-like surface between the two fluids. Both the heavy and light, or as they may be called, the watery and ethery fluids, contain in all cases less or more of all the three ingredients. They seem to vary in their specific gravities according to this law; whenever the upper fluid is extremely light, the under one is extremely heavy; namely,

about 0·72 and 0·98 respectively; and whenever the under fluid is extremely light, then the upper one is extremely heavy, but the two never approximate nearer than 0·93 and 0·82 respectively. As far as I have found, I am pretty well convinced that in this last case the heavy fluid is constituted of 1 atom of ether, 1 of alcohol, and 5 of water; and the light fluid of 1 ether, 1 alcohol, and 1 water, being a true ternary compound of the three elements. These facts are beautifully exhibited by a single experiment. Let equal volumes of pure ether and water be agitated together; on subsiding, the very heavy and very light fluids are immediately perceived; let then pure alcohol be added by degrees, and agitated; it will be observed that both fluids have increased in volume upon each addition, till at length the upper fluid arrives at its maximum volume and specific gravity. A further addition of alcohol then diminishes the volume of ether till at length it disappears, and the whole becomes one uniform fluid.

The boiling point of ether I find forms a curious part of its history; I mean that point of temperature when its vapour is of sufficient force to balance the weight of the atmosphere. In my early experiments I found the point by immersing a thermometer in the boiling fluid, when it stood at 102°; but in subsequent experiments I used a barometer tube bent about one third from the sealed end, and the legs laid parallel. A small portion of ether was let up to the sealed end, and the tube from thence to a little past the turn was filled with mercury. The instrument thus prepared was immersed in a tall jar of warm water till the vapour arose from the ether and depressed the mercury, which ascending in the other leg, was brought to a level in the two. In this way, the same ether, in the temperature of 98°, exhibited a force equal to the atmosphere. Something like this I find takes place in alcohol of 0·83 specific gravity. It boils in a phial at 176°; but in a tube its vapour is equal to the atmosphere in a temperature of 172°. Pure ether of 0·72 specific gravity boils in the tube at 95° or 96°, as Gay-Lussac has observed; but in a phial I find the thermometer may be raised to 98° in the boiling liquid. The boiling point of a mixture of pure ether and pure alcohol may be made to vary from 96° to 170°; but we cannot infer the boiling point from a knowledge of the proportions of the mixture; it is always much nearer that of ether than the proportions would indicate. Indeed it is the same with alcohol and water, and all similar mixtures. A mixture of equal parts of alcohol and water boils at 183°; whereas by the rule of proportion it ought to boil at 194°. A mixture of four parts ether and three parts alcohol I found boiled at 117° in the tube, and 122° or 123° in the air, which by proportion should have boiled at 127°. It was of specific gravity 0·769, and might, therefore, be considered as between the second and third quality.

The modifications of the boiling point of ether produced by

water, however, are the most astonishing. The heavy fluid arising from the washing of ether by water, which is of the specific gravity 0·96, and which consists of 8 or 10 parts of water and 1 or 2 of ether and alcohol, boils at 103° in the tube; but if the temperature be increased, it soon ceases to manifest the increasing progressive elasticity of pure ether, as may well be expected. The reason of this is pretty obvious; water possesses little or no affinity for ether; it yields readily the few atoms it possesses to the influence of heat, and when they are raised, the supply ceases. Hence we see the necessity of using a pure ether when the tension at various successive temperatures is to be found.

Specific Gravity of Ether Vapour.

In 1803 and 1804 I made a great many experiments on the combustion of ether vapour mixed with oxygen gas by electricity. These sufficiently demonstrated the great specific gravity of this vapour, as it was sufficient to have four or five per cent. of volume of it to produce abundance of carbonic acid, and to require a greater abundance of oxygen. I found it expedient to ascertain as near as possible the exact specific gravity, and attempted it as follows in September, 1803.

I took a balloon glass, of the capacity of 253 cubic inches, having a wide neck, to which was adapted a brass cap and stop-cock. Into this a graduated tube, $\frac{3}{10}$ths of an inch diameter, containing ether of 0·758 specific gravity, and a manometer were introduced; the manometer was as usual a tube of $\frac{1}{15}$th inch bore, closed at one end and duly graduated, with a globule of mercury sliding in it. The vessel was immediately made air tight, and kept so for several days, during which time the progress of the evaporation and of the gauge was occasionally noted. The temperature of the air in the room was usually about 55°; but as this was of no importance, it was not particularly noted. The observations follow: the ether tube was graduated into water grain measures: barometer 30 inches.

			Manometer.	Measures of ether evaporated.
Sept.	23	2 p.m.	885	0·0
		5 ——	868	6·5
		8 ——	858	10·0—
	24	1 a.m.	848	16·5
		9 ——	830	20·5
		3 p.m.	825	24·6
		10 ——	818	28·5
	25	1 p.m.	800	34·0
		12 ——	795	38·9
	26	2 p.m.	790	42·0—
		9 ——	780	46·5
	28	9 a.m.	772	49·5

Now 49·5 measures of ether = 37·5 gr. and this quantity being by the manometer = $\frac{113}{772}$ of the atmospheric pressure, we have 113 : 37·5 :: 772 : 256 gr. the weight of 253 cubic inches of ethereal vapour of atmospheric force; but the weight of the same volume of common air = 77 gr. Hence ethereal vapour = 3·3 times the specific gravity of air.

I find amongst my notes in 1805 a similar experiment, from which the specific gravity was deduced = 2·65 only. This difference occasioned me to repeat the experiment as follows:

Balloon containing 404 *Cubic Inches* = 123 *Gr. of Air.*

Barometer, 30 inches.
Ether, 0·728 specific gravity in the temperature 48°.

			Manometer.	Measures of ether evaporated.
1819.—Feb. 25	10	a.m.	 4100	..... 0·0
	1	p.m.	 4052	..... 8·0—
	$2\frac{1}{4}$	——	 4040	..... 9·5
	3	——	 4025	..... 11·0—
	$5\frac{1}{4}$	——	.... 4000+	..... 13·5
	7	——	 3990	..... 15·0
	9	——	 3966	..... 17·0
26	9	a.m.	 3908	..... 25·0
	11+	——	 3903	..... 27·0—
	2	p.m.	.... 3900—	..... 28·0
	6	——	 3881	..... 30·0
	9	——	 3870	..... 32·0
27	9	a.m.	 3824	..... 36·0
	9	p.m.	 3812	..... 39·0

At this period the cock was turned, and the air and vapour let out, till the equilibrium was restored with the atmosphere, the barometer being then 29·5; the thermometer was not noted. In a few minutes the cock was again turned, and the experiment continued.

			Manometer.	Measures of ether evaporated.
Feb. 27	$9\frac{1}{2}$	p.m.	 4077	..... 0·0
28	2	——	 4040	..... 5·5
	9	——	 4025	..... 7·5
March 1	9	a.m.	 4006	..... 10·0
	9	p.m.	 3985	..... 14·0
2	9	a.m.	 3969	..... 15·5
	9	p.m.	 3950	..... 18·0—
3	9	a.m.	 3937	..... 19·5
	9	p.m.	 3919	..... 22·0
4	9	a.m.	 3908	..... 24·0
	9	p.m.	 3890	..... 25·0

			Manometer.	Measures of ether evaporated.
March 5	9	a.m.	3885	27·0
6	9	——	3874	28·0
	9	p.m.	3874	28·0+
7	9	a.m.	3874	28·0+

For the last two days there was only a drop of fluid left at the bottom of the tube (nearly five inches deep) which seemed to be not evaporable; but it was judged proper to continue the experiment in order to ascertain whether the vessel was perfectly air tight, and of course the gauge would continue stationary. The drop of fluid smelled of alcohol, and when diluted and treated with muriate of barytes was milky.

By making the calculation as above, the specific gravity of ether vapour from the first part of the experiment comes out 3·05, and from the last part, 3·2. The slow manner in which ether evaporates in these circumstances is surprising; in the latter part of the experiment it is to be ascribed to the depth of the surface of fluid in the tube, and the partly saturated air.

Though convinced the above results were very good approximations, I was desirous to have a confirmation of it by some more direct method. I took a bottle of the capacity of 2,600 gr. of water, and graduated accordingly; this being filled up to 1,100 gr. with dry mercury was inverted in the mercurial trough with 1,500 common air. Through this mercury were passed 1, 2, 3, or more grains of ether, which expanded the air, and from the quantity of expansion, compared with the weight of ether let up, the specific gravity of the vapour was inferred. This method did not give uniform results owing to a considerable portion of such minute quantities of ether being entangled by the mercury in its passage. To remedy this, I took a small tube, one-seventh of an inch in diameter internally, and two inches long, which was sealed at one end, and then graduated into water grains, which was such as to allow nearly one-fourth of an inch for one grain. This was filled with mercury, except for one, two, or more grain measures, which were afterwards filled with ether, and the finger being applied, the tube was plunged into the mercury and passed through the neck of the bottle up to the surface of the mercury in the bottle. In this way the ether was conveyed through the mercury without quitting the tube, and by gentle agitation was ejected and dissipated in vapour in a few minutes afterwards. The results in several experiments were nearly uniform, giving an increase of volume of gas from 255 to 275 grain measures for each grain of ether in weight. This gives the specific gravity of ether vapour from 3·1 to 3·3. On the whole, I think 3·1 is probably the nearest expression in two places of figures that can be attained.

Elasticity of Ether Vapour, the same in Air and in a Vacuum.

The same tension or elasticity of ether vapour takes place in air as in a vacuum, just as with the steam of water and other liquids. But this is not true of impure ether, if it be made to pass through water into the air, because by this operation it is improved in quality, though greatly diminished in quantity.

When the temperature of the air was 43°, and barometer 29·70, I passed up through water into a graduated tube containing 51 grain measures of air, about three or four grains of 0·73 ether. The air was in a few minutes expanded to 74 measures; and the ether barometer (that is, a barometer with the same kind of ether thrown up into the vacuum) stood at 20·5 in the same temperature; hence we have $\frac{29{\cdot}7}{20{\cdot}5} \times 51 \left(\frac{p}{p-f} \times 51\right) = 74$ nearly; which accords with the before-mentioned theorem. The tube being afterwards immersed in water of 66° gave 104 measures of vapourized gas; and in 70° gave 118 measures. It stood for some months in water, still retaining a fluctuating volume of gas, according to the changes of barometer and thermometer; and at last the gas was passed through water, and instantly gave the original 51 measures of air.

The quality of ether may be judged of from passing a small portion of it through water in a graduated tube. Thirty grain measures of the best ether (0·73) passed up a tube of eight inches long filled with water lost four or five gr. Thirty grains of another ether, consisting of a mixture of 15 ether (0·735) and 15 alcohol (0·85), when passed in like manner, only gave five measures of fluid ether, swimming on the surface of the water.

Relation of Ether Vapour to Liquids.

Gases vapourized by ether may be kept over dry mercury, and transferred through the same without loss. But they are not kept over water, alcohol, and other liquids, without loss of vapour, though this is variable according to the nature of the fluid and other circumstances.

Alcohol absorbs ether vapour out of air much faster than water does. I filled two similarly graduated tubes with etherized air, and placed them over alcohol and water respectively: they lost vapour as under:

Tube over alcohol.	Tube over water.
155 measures.	155 measures.
116 in 5 minutes.	142 in 10 minutes.
112 in 8 minutes.	138 in 13 minutes.
104 in 30 minutes.	130 in 30 minutes.
100 washed.	100 washed.

The non-efficiency of water in abstracting ether vapour is further manifested by the following experiment.

I took a tall graduated cylindric jar, of three inches diameter, into which 20 oz. measures of air were passed over water. Thirty grain measures of ether (0·73) were then passed up into the air, through a volume of five inches of water, which was of course diminished a little in its passage, and then spread over the surface of the water to the thickness of $\frac{1}{200}$th of an inch nearly. The volume of air and vapour varied as under:

H.	M.		Oz.
—	—	.....	20
—	3	.....	$22\frac{1}{2}$
—	6	.....	24
—	12	.....	26
—	20	.....	$27\frac{1}{2}$
—	26	.....	$28\frac{1}{4}$
—	32	.....	$28\frac{1}{4}$
—	50	.....	28
2	27	.....	27
1 Day		.....	23
1 Week		.....	$21\frac{1}{2}$
		Washed.	20

Here it is observable, the vapour increased for half an hour, and then began to decline again, but slowly. It increased the volume by $8\frac{1}{4}$ oz. = 3,960 grain measures, which is equal to 15 gr. in weight by the preceding determination; but the ether weighed 22 gr.; so that a loss of one-third of the weight of the ether only was occasioned by the action of so great a surface of water on it for half an hour.

Force of Ether Vapour.

My former experiments on the force of ether having been made with an article not of the highest purity, they ought all to exhibit a force *too low* for the temperature. Such I find to be the fact; at least within a range of temperature of easy investigation, that is, from 30° to 140°. The difference, however, is but small, and may, without much error, be corrected by deducting 2° or 3° from the respective temperatures, as given in my table. (New System of Chemistry, p. 14.) The apparatus to be used, consists of a common barometer tube, one bent into a syphon at one-third of the length from the sealed end, and a tall smaller one bent six or seven inches from the sealed end, and having the other leg 40 inches long. The first of these instruments is best used for atmospheric temperatures, having a drop of ether let up into the vacuum. The second, is to have its short leg filled with mercury, and an inch of the other leg, a drop of ether being at the top of the mercury in the short leg.

This is used from temperature 80° to 110° or 120°. The third is to have its short leg filled with mercury, and a drop of ether as the other, and its long leg filled to various heights with mercury, according to the temperature. It may be advantageously used from 120° to 140°. For temperatures between 140° and 212°, I have always used a tube similar to the last mentioned, but having its upper extremity sealed, and containing air of common density over the mercurial column, and nearly equal in volume to the capacity of the other leg. When the ether vapour is formed in force, it condenses the said air, and from the condensation, the force is inferred by a well-known law. Having had some reason to suspect my former results by this instrument were somewhat too high; I have been induced to examine the defects to which this instrument is liable. The end of the tube must be drawn out to a point before sealing, and suffered to cool to the temperature of the air; after this, the end must be closed by the point of a flame, otherwise the air in the tube may be rarefied by the heat, in which case the force of the steam will be overrated. Another cause of similar error is the existence of ether vapour in the air at the moment of sealing; this will happen if the tube is not carefully dried inside after the instrument is filled with mercury. In this case, the air in the tube is rarefied by the steam, and consequently is of an unknown but reduced density. The opposite error is liable to be induced, by the frequent use of the instrument. By the motion of the mercury, the small remains of ether mechanically mixed with it rises to the top, and a visible stratum of ether is thereby exposed to the air. In this case an addition of force is given to the air; but as the quantity of this force is known for any temperature, it may be allowed for accordingly. I prefer, however, sealing the tube when well dried, and the air of atmospheric density at the time; and if the ether appear to rise to the surface afterwards, the correction must be applied. In order to have a complete check upon this instrument, it should be adapted so as to be applicable at some temperature (as 140°), where the force is known by other direct means. The error, if any, will thus be shown, and may be calculated for other temperatures.

I have lately made, for the first time, various experiments on the force of steam from water, in temperatures from 212° to 300°; the results which convince me that the theoretic forces which I gave in the fifth volume of the Memoirs, as also those subsequently in my Chemistry, are both erroneous; the former being about as much too small as the latter are too large, so that the mean of the two series is a near approximation to the truth.

Experiments on the force of aqueous steam in high temperatures have been lately made by Mr. Southern, of the Soho, Birmingham,* and by Dr. Ure, of Glasgow,† the results of

* Dr. Robison's Works by Dr. Brewster.

† It would have given me great pleasure to have been able to adduce Dr. Ure's

which agree very well with each other, and with the mean of my two theoretic tables. As for the force of steam below 212°, no one has found any material variation from those in my first table; indeed scarcely any one seems to have attended much to those below 100°, which I was most anxious to have correct. The force of steam at 32° is an important element; I have spent much time and labour upon it, both before and since my first table was published; it is not less, I think, than 0·2 of an inch, nor more than 0·3; these being the extremes of my experiments; perhaps 0·25 is very near the truth.

My table of the force of alcoholic vapour represents it too high for temperatures below 60°, and for those above rather too low. These errors arose partly from the alcohol not being free from water, and partly from a mistake, as I now apprehend, in fixing a standard mark on the alcohol barometer. They are but small, and of little importance, as the observations were not used in establishing general principles. An improved and more extended series of observations on the force of alcohol vapour has recently been published by Dr. Ure, as mentioned above, the results of which fall in as well as can be desired with those from water, in establishing a general law that the vapours of homogeneous liquids expand in geometrical progression to equal intervals, or at least to *the same* intervals of temperature. I may add, my own experiments recently made for the first time, corroborate those of Dr. Ure in the interval of temperature from 175° to 212°.*

The following skeleton of a table of the force of vapour from water, alcohol, and ether, is formed from what I consider as the most correct experiments hitherto made on these subjects, and may have its use, though it will be found not to differ very materially from my former tables, except where they differ from each other.

experiments on ether also, in corroboration of my early experiments, and of the general principles thence derived; a stronger condemnation of those principles could not have been brought forward than their agreement with the results of Dr. Ure on ether vapour. All the information we have given as to the quality, &c. of his ether is contained in the following paragraph. "The ether of the shops, as prepared by the eminent London apothecaries, boils generally at 112°; but when washed with water or redistilled, it boils at 104° or 105°. It may by rectification, however, be made to boil at a still lower temperature." We are presented with two series of experiments on the force of ether vapour; the first begins at 34° with the force 6·2, and ends at 104°, with the force of 30 inches of mercury; the second begins at 105° with the same force, and ends at 210° with the force of 166 inches. What the specific gravities of the two kinds of ether used were, and whether the ethers used were obtained from the very inferior ether of 112° by washing, or by distillation, are important points, concerning which we are not informed. However, Dr. Ure contrives to blend these two disjointed series, and to compare the results with those of mine made upon ether which boiled at 98°; and finding great discrepances, he concludes my results on ether and principles deduced from them are pregnant with errors.

* Philosophical Transactions, 1818.

Table of the Forces of Aqueous, Alcoholic, and Ethereal Vapours.

Temperatures (common scale).	Aqueous vapour. Ratio, 2·6.	Alcohol vapour. Ratio, 2·7.	Ethereal vapour. Ratio, 2.
36°	0·29 in.	0·56 in.	7·5 in.
64	0·75	1·51	15·0
96	1·95	4·07 (*f*)	30·0
132	5·07 (*a*)	11·00 (*g*)	60·0
173	13·18 (*b*)	29·70 (*h*)	120·0
220	34·20 (*c*)	80·20 (*i*)	240·0
272	88·90 (*d*)	—	—
340 (*e*)	231·00	—	—

Dr. Ure's numbers for ether corresponding to the above, the last exclusive, are 6·55, 13, 25·7, 49·8 [49], 96·4; the ratio is of course less than two, and a descending one; namely, 1·98, 1·97, 1·94, and 1·93; this last circumstance characterizes a mixed liquid.

I have not extended the experiments on ether further than 212°; but as that temperature gives a force of 207 or 209, I estimate the force to be 240 at 220° nearly.

If the forces registered in the preceding table be allowed as near approximations to the truth, it must, I think, be admitted that they increase in geometrical progression to the same intervals of temperature for a range of 200° at least. Whether those intervals of temperature are equal one to another successively is another inquiry, which the above facts and observations do not enable us to decide.

Analysis of Ether by Electricity, &c.

When a little fluid ether is let up into Volta's eudiometer, either over mercury or water, and a small portion of azotic gas is likewise sent up, in order to be vapourized by the ether; then if the vapourized air be electrified for an hour, some permanent gas is produced, and charcoal is precipitated. The gas when washed is chiefly or wholly carburetted hydrogen; for it takes two volumes of oxygen, and yields one of carbonic acid gas. If the vapourized gas be dry and over mercury, a volume of vapour yields two volumes of carburetted hydrogen, and moisture is perceived within the tube. If the electrification were continued.

(*a*) Southern, 4·71. Ure, 4·70
(*b*) Southern, 13·00. Ure, 12·95.
(*c*) Southern, 35·20. Ure, 35·50.
(*d*) Southern, 88·00+. Ure, 89·00.——90. The mean of my two tables.
(*e*) This observation is Mr. Southern's. There is reason to suspect his temperatures too high for his forces in the high pressures. They exceed Dr. Ure's.
(*f*) Ure, 4·02.
(*g*) Ure, 11·20.
(*h*) Ure, 30·00.
(*i*) Ure, 78·50. Bettan, 82.

no doubt the volume of gas would be greatly increased, and end in pure hydrogen mixed with azote.

These experiments are not decisive; but they evidently point out the composition of the atom of ether to be 1 carburetted hydrogen, 1 charcoal, and 1 water, or 2 olefiant gas, and 1 water.

The best method of analysis is by firing the vapour of ether mixed with oxygen gas in Volta's eudiometer. This method I discovered in September, 1803, and have used it occasionally ever since. It may be proper to describe the various modifications of which this process is susceptible.

When a few drops of ether are passed through water into the eudiometer containing oxygen gas, the volume of the gas is in a few minutes enlarged more or less, according to the temperature.

In temperatures from 60° to 70°, the volume is about doubled; but below those it is less than doubled; and above more than doubled, agreeably to the principle before explained.

(*a*) If the air be doubled or more, and an electric spark be taken in it, the probability is, that no explosion will ensue; if by repeated sparking an explosion take place, it is feeble, and may be repeated a few seconds afterwards, sometimes once or twice. The residue of gas being examined is found to contain a little carbonic acid, some new combustible gas, and oxygen in various proportions. In short, the operation is very incomplete, owing to an excess of ether vapour.

(*b*) If the oxygen gas be good, and the volume be increased from 100 to 150 by the vapour (which will naturally arise in temperatures between 40° and 50°, and in higher temperatures the volume may be reduced by cautious agitation, till the water has absorbed part of the superfluous ether and vapour), then a spark produces a violent explosion. The gaseous volume is doubled, or from 150 becomes 300; and upon examination is found to consist of carbonic acid and new combustible gas, but chiefly the latter. Little or no oxygen is found.

If the ether vapour be only from 3 to 10 per cent. of the volume of oxygen, the explosion is vigorous, and a complete combustion takes place. The residue consists of carbonic acid and oxygen gases only. Ten volumes of ether vapour require about 60 of oxygen, and produce about 40 of carbonic acid.

(*c*) If 100 oxygen be increased by ether vapour to 120 or 130, a violent explosion ensues, and the whole of the vapour is converted into carbonic acid, water, and new combustible gas; a little charcoal is sometimes deposited, so as to make the air muddy at the instant after explosion; no oxygen is found in the residue.

(*d*) The combustion of ether vapour may be effected by common air as well as by oxygen gas, only the proportion of vapour to air is very small and limited. If the vapour exceed five per cent. it will not fire; and if it fall short of two per cent. it rarely fires. The combustion is attended with the production of new combustible gas, or otherwise complete, according to the

greater or less proportion of vapour, as is the case with oxygen gas.

In respect to the *new combustible gas* in the above paragraph, its nature may be ascertained by abstracting the carbonic acid in the usual way, and then exploding it with oxygen. In the paragraph (*a*), the new gas is often nearly pure carburetted hydrogen; but in (*c*) and (*d*) it is always a mixture of carbonic oxide and hydrogen in nearly equal volumes; as is proved from its requiring 50 per cent. of oxygen, and producing 50 per cent. of carbonic acid. In (*b*) it is chiefly these two gases, but has a little carburetted hydrogen occasionally mixed with them.

When a certain volume of ether vapour is completely burned at one operation, or it is partially burned at the first, as in (*a*), (*b*), (*c*), and (*d*), and the combustion finished by a second operation, still the same volume of vapour requires the same volume of oxygen for its complete combustion, and produces the same volume of carbonic acid. And it is always found that the carbonic acid contains two-thirds of the oxygen spent, and consequently the hydrogen engages one-third of the oxygen to form water. Hence it appears that the combustible element of ether is olefiant gas; but as there is reason to conclude that oxygen is one of the elements of ether, it must be combined with hydrogen; so that water must be the incombustible element.

In order to find what number of atoms of water and olefiant gas must be combined to form one of ether, we must have regard to the *weights* of the different elements which combine. Now, from the experiments above related, it appears that one measure of ether vapour (weighing 3·1) requires six measures of oxygen gas (weighing 6·6); but two atoms of olefiant gas weigh 12·8, and one of water weighs 8, making together 20·8, which would require six atoms of oxygen, weighing 42, for their combustion; that is, such compound atom would require rather more than double its weight of oxygen, which is the proportion I find by experiment for ether vapour. Hence then we may conclude, that the atom of ether weighs 20·8, and is compounded of one atom of water and two of olefiant gas.

In January, 1809, I made an experiment on the slow combustion of ether in a lamp, in a large balloon glass. The capacity of the balloon was two cubic feet; hence the oxygen of the common air in it would weigh 250 gr. nearly. A small lamp with ether was lighted, and instantly dropped into the balloon, which was immediately closed. The lamp burned till it was extinguished for want of air. After a few minutes it was taken out, and the loss of weight ascertained to be 31 gr. The residuary gas being examined was found to contain 16 per cent. oxygen, and 3 or 4 carbonic acid; but in order to obtain the carbonic acid more accurately, the whole volume of air was subjected to lime water, in such manner that all the air which came out was agitated in the lime water that entered the balloon. The quantity of lime water requisite to saturate the carbonic

acid was as much as saturated 107 gr. in weight of dry sulphuric acid = 60 gr. of carbonic acid = 17 charcoal + 43 oxygen. But the oxygen spent in the combustion was $\frac{5}{21}$ of 250 gr. = 60 gr. nearly, of which we find two-thirds, or rather more, in the carbonic acid produced; the rest must have combined with the hydrogen. And the ether consumed was rather more than one-half of the weight of the oxygen, which may well be supposed to arise from a little loss by evaporation. This experiment, therefore, corroborates the conclusion above obtained.

My first idea of the ether atom, published in the table on the absorption of gases by water in 1803,* was two atoms of carbon and one of hydrogen. This incorrect notion was formed from some of my early experiments combined with the analysis given by others. M. Saussure, in his last essay on ether, has determined its proportions as under; which, being compared with mine, are found to differ from them materially.

	Saussure's.	Mine.
Carbon	67·98	51·9
Oxygen	17·62	33·7
Hydrogen	14·40	14·4
	100·00	100·0

In the present essay I have alluded to the weight of an atom of alcohol; but this weight is not that given in my Chemistry, Part I. From recent experiments on the combustion of alcoholic vapour in oxygen by electricity, as well as from the combustion of alcohol by the platina wire lamp without flame, I believe the alcohol of 0·82 specific gravity is constituted of one atom carburetted hydrogen and one of water, as it seems to give carbonic acid = half the volume of oxygen consumed, or very little more. But there is a remarkable difference in the results when alcohol is burned in a lamp in common air. This combustion gives carbonic acid nearly = two-thirds of the volume of oxygen, and would imply alcohol to be one water and one olefiant gas. At present I have not leisure to clear up this difficulty.

Article VI.

Calculations of Solar Eclipse to take place on Sept. 7, 1820. By Col. Beaufoy, F.R.S.

(To Dr. Thomson.)

MY DEAR SIR, *Bushey Heath, Jan.* 6, 1820.

The annular eclipse which takes place the 7th of next September will naturally engage the attention of Europe; and it

* Memoirs, vol. i. (Second Series.)

being desirable to have corresponding observations on so rare a phenomenon, I have, with the hope of directing the view of others towards this object, sent you my calculations of the *particular* appearances at this place, as well as the *principal* appearances in other parts of the world. By a mean of several observations of the circumpolar stars, made with an excellent circular instrument, two feet in diameter, and constructed by Mr. Cary, I find the latitude of my Observatory to be 51° 37′ 44·27″ N. and longitude W. in time, 1′ 20·93″ instead of 51° 37′ 42″, and 1′ 20·7″ as shown by Hadley's sextant, and an artificial quicksilver horizon. I remain, my dear Sir,

Yours very truly,

MARK BEAUFOY.

Solar eclipse, Sept. 7, 1820.

Bushey Heath, lat. 51° 37′ 44·27″ N.; long. W. in time, 1′ 20·93″

	Apparent Time.
Beginning	0h 21′ 50·0″
Visible conjunction	1 48 23·0
Ecliptic conjunction	1 50 18·6
Greatest obscuration	1 51 12·0
End	3 12 07·0

Nearest approach of centres, 3′ 02″. Digits eclipsed on the sun's northern limb, 10° 28′ 08″. Moon makes the first impression on the sun's disc 54° 48′ from the vertex on the right.

Places on the Earth where the principal Appearances of the Solar Eclipse occur.

Apparent Time at Greenwich.

	A. T. at Greenwich.				Latitude.				Longitude.			
Eclipse begins at sun-rise	11h	22′	07″	A. M.	59°	38′	34″	N	90°	51′	30″	W
Sun rises centrally eclipsed	12	54	09	P. M.	81	35	42	N	148	50	36	W
Sun centrally eclipsed on the meridian	1	08	09	P. M.	75	50	18	N	17	02	07	W
Sun eclipsed at the true conjunction	1	51	39	P. M.	55	00	14	N	6	03	36	E
Sun eclipsed at the middle of the transit	2	01	34	P. M.	51	18	56	N	8	36	02	E
Sun sets centrally eclipsed	3	09	00	P. M.	27	01	21	N	45	49	20	E
Eclipse ends at sun-setting	4	41	02	P. M.	3	15	10	N	20	05	03	E

Duration of the eclipse, 5h 18′ 55″.


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